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# Thermoelectric Power of Bismuth Thin Films

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**Pouvoir thermoélectrique dans les Couches minces de Bismuth**

Un dispositif cryogenique a été fabriqué pour le mesure du pouvoir thermoélectrique et une étude préliminaire a été effectué dans les couches minces de bismuth à la température entre 77 et 300 K. Comme dans les travaux préalables, les Bi films sont préparés par évaporation en vacuum sur des substrats en verre à la température ambiante. Les résultats expérimentaux obtennus montrent que des pouvoirs thermoélectrique sont insensible à la température. Le signe de conductivité, auquel nous avons en un intérêt, fut négatif pour tous échantillons.

## Introduction

Size-quantization of an electronic energy state in bismuth film, known as the quantum size effect, has been studied both experimentally and theoretically. Many observed transport properties show a typical oscillatory behavior with a period of film thickness nearly equal to the de Broglie wavelength as predicted by the theory. In order to have further insight into the transport properties, we have carried out measurements of the resistivity, Hall coefficient, and magnetoresistance on a glass-coated Bi film; the film is prepared by thermal evaportion of Bi onto glass (partly mica) substrate kept at room temperature, in contrast with a heated substrate used by other workers. However, we have not been concerned with the oscillatory behavior because of uncertainty in determining the film thickness.

One of the characteristic features of our experimental results so far obtained[1,2] is that the Hall coefficient $R$ for thinner film with thickness $t < 500$ Å is positive at room temperature and as the temperature is lowered it becomes negative by crossing zero at a certain temperature, whereas for $t > 500$ Å it is always negative. The positive sign of the conductivity type was considered as due to the presence of a local acceptor state. Besides the Hall effect, the polarity ($p$ or $n$ type) can be checked by measuring the thermoelectric power. For this purpose we have constructed a new cryostat and obtained some preliminary results for glass-coated Bi films. Recently Favennec and Contellec[3] have reported the thermoelectric data on Bi and $Bi_x\, Sb_{1-x}$ films discussing

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them in terms of the quantum size effect.

## Experimental

The details of the sample preparation were described in a previous work; in effect thermal evaporation of Bi onto a glass substrate kept at room temperature, the sample shape being of the same form as used for the Hall effect. Figure 1 shows a cryostat for the thermal measurement in a steady state. The substrate was clamped at both ends by copper blocks, on which a heater of manganine wire was noninductively wound and fixed by araldite. The thermocouples (copper-constantan) were soldered by Wood's metal in 0.5mm holes of the blocks drilled close to the sample.

For good electrical and thermal contact, the both ends of the Bi films were wetted by gallium. The lower block was in contact with the bottom of the container, which was evacuated in vacuum around $10^{-6}$ Torr. The temperature at both ends was measured by a dc potentiometer and the emf across the sample was read by a high sensitivity microvolt-meter. Parasitic emf's in the measuring circuit were measured and corrected for. Helium gas was occasionally filled in the container for good thermal equilibrium.

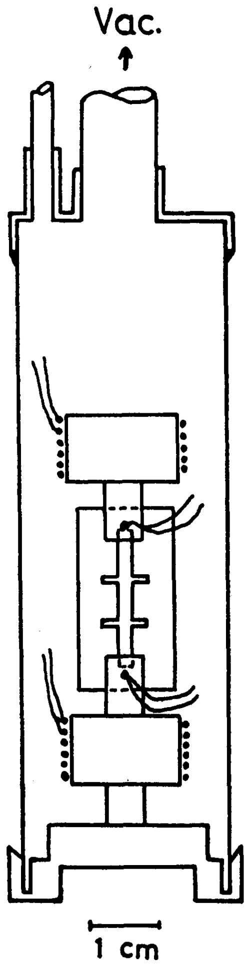


Fig. 1. Arrangement expérimentale pour des mesures du pouvoir thermoélectrique dans couches minces de bismuth. L'échantillon est cramponnée par des blocs de cuivre, dans lesquels les couples thermoélectrique de "cuivre-constantantan" sont attachée avec Wood's metal.

## Results and discussion

In this steady state measurement, the upper end of the sample was usually kept at higher temperature than the lower end; the linear dependence of the emf on the temperature difference $\Delta T$ between the two ends was examined to be satisfied at each temperature. In Fig. 2 are shown the typical variations of measured emf voltage $V$ at 293 and 77 $K$ with increasing the difference $\Delta T$, where no correction for $V$ is made. It is seen that the proportionality is well established; the slope of this straight line yields the thermoelectric power $\alpha$ for the respective temperatures.

The temperature dependence of $\alpha$ is shown in Fig. 3 for a few samples; the value of polycrystalline Bi measured by Tanuma[4] is also indicated by a dotted line for comparison. We note further the anisotropic values of pure bulk Bi at room temperature:[5] the component perpendicular to the trigonal axis $\alpha_{\perp}=-54\mu V$/deg and the parallel component $\alpha_{\parallel}=-110\ \mu V$/deg. The observed thermoelectric power of thin films is thus indicative of the fact that the trigonal axis is perpendicular to the plane of the grown film, as already pointed out by Favennec and Contellec.[3] Since the present data are limited, we cannot see how the value $\alpha$ depends on the film thickness; $\alpha$ for films is seen to be smaller than the bulk value. It is to be noted that the power is negative in its sign over the temperature range studied; this was confirmed even at liquid helium temperature, although the absolute value of $\alpha$ was not determined because of lack of enough sensitivity of the thermocouple used. On the contrary, the Hall coefficient for thin films with thickness $t<500$ Å was positive at room temperature. The difference of the sign of the conductivity revealed by the two experimental methods is quite interesting.

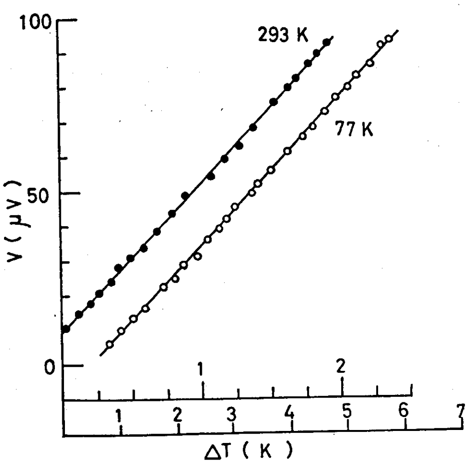


Fig. 2. Proportionnalité du voltage thermoélectrique $V$ mesurée par un microvolt-metre du différence de la température $\Delta T$ à des deux bouts de l'échantillons; le haute échelle pour 293 K et le bas celle pour 77 K.

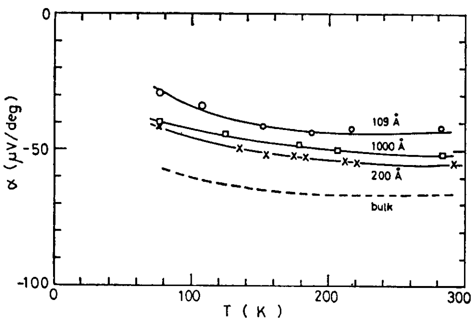


Fig. 3. Variation du pouvoir thermoélectrique $\alpha$ en fonction de la température pour quelques échantillons.

The temperature variation of $\alpha$ in Bi films is seen to be similar to that in bulk Bi (see dotted line). Above 150 K it is almost temperature-independent; it is known that the temperature-independence of the thermoelectric power is characteristic of a typical semimetal having a zero Fermi energy.[6] A theoretical expression of $\alpha$ or the Seebeck coefficient can be referred to many references. Our experimental studies are still in progress and these will be discussed later by considering the band structure of Bi films (semimetal or semiconductor) on the basis of classical and quantum transport scheme.

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